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[Title of the Invention] STACKED PHOTOVOLTAIC ELEMENT AND
METHOD FOR PRODUCING THE SAME

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[Title of the Invention] Stacked Photovoltaic Element

5 and Method for Producing the Same

[Claim(s)]

[Claim 1] A method for producing a stacked
photovoltaic element comprising an intermediate layer
between photovoltaic elements each having a PN- or PIN-
10 junction, characterized in that a first layer mainly
composed of indium oxide is stacked on at least one
interface with the photovoltaic element and then a
second layer mainly composed of zinc oxide is stacked
on the first layer to form the intermediate layer.

15 [Claim 2] The method according to Claim 1 for
producing a stacked photovoltaic element, characterized
in that the second layer is formed to be thicker than
the first layer.

[Claim 3] The method according to Claim 1 or 2
20 for producing a stacked photovoltaic element,
characterized in that the first layer is formed to have
a thickness of 1 nm or more and 50 nm or less.

[Claim 4] The method according to any one of
Claims 1 to 3 for producing a stacked photovoltaic
25 element, characterized in that the second layer is
formed at a rate higher than that of the first layer.

[Claim 5] The method according to any one of

Claims 1 to 4 for producing a stacked photovoltaic element, characterized in that the second layer is formed at a temperature lower than that of the first layer.

5 [Claim 6] A stacked photovoltaic element comprising an intermediate layer between photovoltaic elements each having a PN- or PIN-junction, characterized in that the intermediate layer comprises a first layer and a second layer stacked in this order
10 on at least one interface with a photovoltaic element, the first layer being mainly composed of indium oxide and the second layer being mainly composed of zinc oxide.

 [Claim 7] The stacked photovoltaic element
15 according to Claim 6, characterized in that the second layer is thicker than the first layer.

 [Claim 8] The stacked photovoltaic element according to Claim 6 or 7, characterized in that the first layer has a thickness of 1 nm or more and 50 nm
20 or less.

 [Claim 9] The stacked photovoltaic element according to any one of Claims 6 to 8, characterized in that the second layer has a higher transmittance than the first layer at a wavelength of 800 nm.

25 [Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a stacked photovoltaic element in which at least two photovoltaic elements having a PN- or PIN-junction are stacked and an intermediate layer is provided between the elements,
5 and a method for producing the same.

[0002]

[Prior Art]

A photovoltaic element is a device which converts incident light energy into electric energy. Among such
10 devices, a solar cell is a photovoltaic element which converts solar rays into electric energy. It is characterized by efficiently converting light over a wide wavelength range into electric energy. It is necessary to efficiently absorb light over a wide
15 wavelength range in order to achieve a high conversion efficiency.

[0003]

A stacked photovoltaic element, which is formed by stacking a plurality of photovoltaic elements each
20 containing a photoactive layer having a different band gap from each other is known as one of the solutions to achieve a high conversion efficiency. This stacked photovoltaic element has one photovoltaic element having a photoactive layer of larger band gap on a
25 light incident side or thinner photoactive layer, and another photovoltaic element having a semiconductor of smaller band gap or thicker photoactive layer in this

order from the light incident side, the former
absorbing light of shorter wavelengths and the latter
absorbing light of longer wavelengths which the former
transmits. The stacked photovoltaic element,
5 therefore, can more efficiently absorb and utilize
light over a wider wavelength range.
[0004]

It is essential to provide each photovoltaic
element having a photoactive layer having a different
10 band gap with light of a wavelength in a range suitable
for that element, because a wavelength range of
incident light which each photovoltaic element can
utilize varies depending on the band gap of a
semiconductor used as the photoactive layer for that
15 element. In other words, photon cannot be absorbed by
the semiconductor when photon has lower energy than the
band gap of the semiconductor. In such a case, it only
passes through the semiconductor without being
utilized. On the other hand, photon having higher
20 energy than the band gap of the semiconductor cannot be
fully utilized although it can be absorbed, because
potential energy of electron which can be produced when
the electron is excited is limited by magnitude of the
band gap, whereby the difference between the band gap
25 energy and photon energy cannot be utilized. It is
therefore essential to design a stacked photovoltaic
element to selectively introduce light of shorter

wavelength range into a photovoltaic element on the incident light side and light of longer wavelength range into another photovoltaic element arranged under the above element.

5 [0005]

One of the known solutions is to provide an intermediate layer as a light-reflecting layer between these photovoltaic elements. For example, Patent Document 1 or Non-patent Document 1 disclose a method
10 for providing an electroconductive intermediate layer each between the elements which reflects light of shorter wavelength and transmit light of longer wavelength. Patent Document 2 discloses a method for using an intermediate layer, which is a multiple-layer
15 film structured by stacking two or more materials alternatively, to provide a conductive layer, which reflects light of shorter wavelength and transmits light of longer wavelength between the elements.

[0006]

20 [Patent Document 1]

Japanese Patent Application Laid-Open No. S63-77167

[Patent Document 2]

Japanese Patent Application Laid-Open No. 2001-
25 308354

[Non-patent Document 1]

Kenji Yamamoto, "Thin-film polycrystalline silicon

solar cell", Applied Physics, The Japan Society of Applied Physics, May, 2002, Vol.71, No.5, p.524 to 527 [0007]

[Problem to be Solved by the Invention]

5 As discussed above, the extensive studies on intermediate layers have produced the intermediate layers good to some extent. However, there are problems to be solved to satisfy the demands for improved optical and electrical characteristics,
10 compatibility with a semiconductor layer, and deposition rate.

[0008]

 For example, the method disclosed by Patent Document 2, although giving a selective reflection
15 layer structure satisfying the light reflection and light transmission characteristics, is found to be still insufficient in producing the intermediate layer having no adverse effect on the photovoltaic element and having good connection with the photovoltaic
20 element. For the intermediate layer to have sufficient characteristics, the following technical requirements should be satisfied.

[0009]

 The intermediate layer should be kept in good
25 ohmic contact with the semiconductor layer under the intermediate layer. It should be formed in such a way to cause little damages to the underlaying

semiconductor layer by chemical modification (e.g., by
oxidation) or physical modification (e.g., by ion-
caused damages). Moreover, it should have an adequate
resistivity and film thickness, and should be designed
5 to control lateral flow of shunt current via the
intermediate layer.

[0010]

It is an object of the present invention to
provide a stacked photovoltaic element of high
10 conversion efficiency, capable of efficiently
collecting energy over an entire wavelength range of
incident light, and having good open-circuit voltage
(Voc) and fill factor (FF), among others and a method
for producing the same in consideration of the above
15 problems.

[0011]

[Means for Solving the Problem]

The present invention has been accomplished by the
extensive studies to solve the above problems, and has
20 the following constitutions.

[0012]

The present invention is a method for producing a
stacked photovoltaic element comprising an intermediate
layer between photovoltaic elements each having a PN-
25 or PIN-junction,

characterized in that a first layer mainly
composed of indium oxide is stacked on at least one

interface with the photovoltaic element and then a second layer mainly composed of zinc oxide is stacked on the first layer to form the intermediate layer.

[0013]

5 In the above-mentioned method for producing a stacked photovoltaic element, it is preferable that the second layer is formed to be thicker than the first layer.

[0014]

10 It is also preferable that the first layer is formed to have a thickness of 1 nm or more and 50 nm or less.

[0015]

 It is further preferable that the second layer is
15 formed at a rate higher than that of the first layer.

[0016]

 It is further preferable that the second layer is formed at a temperature lower than that of the first layer.

20 [0017]

 The present invention is a stacked photovoltaic element comprising an intermediate layer between photovoltaic elements each having a PN- or PIN-junction,

25 characterized in that the intermediate layer comprises a first layer and a second layer stacked in this order on at least one interface with a

photovoltaic element, the first layer being mainly composed of indium oxide and the second layer being mainly composed of zinc oxide.

[0018]

5 In the above-mentioned method for producing a stacked photovoltaic element, it is preferable that the second layer is thicker than the first layer.

[0019]

 It is also preferable that the first layer has a
10 thickness of 1 nm or more and 50 nm or less.

[0020]

 It is further preferable that the second layer has a transmittance higher than that of the first layer at a wavelength of 800 nm.

15 [0021]

[Embodiment(s)]

 The preferred embodiments of the present invention are described by referring to the attached drawings. It should be understood that the present invention is
20 not limited to these embodiments.

[0022]

 A solar cell comprising two photovoltaic elements will be described as an example of the stacked photovoltaic element of the present invention.
25 However, the present invention is not limited to this structure, and can be applied to a stacked photovoltaic element comprising three or more photovoltaic elements.

[0023]

First, the intermediate layer as the feature of the present invention is described. In the present invention, a stacked photovoltaic element is formed by
5 stacking a plurality of photovoltaic elements each containing a PN- or PIN-junction, wherein a first layer mainly composed of indium oxide is stacked on at least one interface with a photovoltaic element and then a second layer mainly composed of zinc oxide is stacked
10 on the first layer to form the intermediate layer. The stacked photovoltaic element of the above structure brings the following effects. The structure and each component of the stacked photovoltaic element of the present invention will be described in detail later.

15 [0024]

Incorporation of the intermediate layer of the above structure can prevent deterioration of the Voc and FF values, and allows the stacked photovoltaic element to exhibit the excellent characteristics for
20 extended periods of use. The Voc and FF values tend to deteriorate, when an intermediate layer of zinc oxide alone is provided on the interface with the photovoltaic element, while depending on conditions under which zinc oxide is produced, its resistivity and
25 thickness, among others. This phenomenon is not notably observed when a photovoltaic element is provided on zinc oxide. For example, zinc oxide may be

used for a reflection layer to be provided on a substrate type photovoltaic element. In such a case, deterioration of the Voc or FF characteristics is not observed notably, from which it is considered that the
5 deteriorated characteristics result from the process itself for forming the zinc oxide layer on the interface with the photovoltaic element. In other words, it is conceivably related to the process in which the semiconductor is formed on zinc oxide in a
10 reducing atmosphere whereas zinc oxide is formed on the interface with the photovoltaic element in an oxidative atmosphere: oxygen in zinc oxide formed on the interface with the photovoltaic element is depleted by the atom on the interface with the photovoltaic element
15 to oxidize the semiconductor, resulting in formation of a modified layer in the interface between the photovoltaic element and zinc oxide.

[0025]

The above tendency is more noted when the zinc
20 oxide layer is formed in the presence of oxygen or moisture. Its characteristics are further deteriorated when the film formed by sputtering or the like, which generates the oxygen ion, because of the ion-caused damages to the interface with the photovoltaic element.
25 The phenomenon is still more noted when the zinc oxide layer is formed on a p-type layer, which is more sensitive to the Voc characteristics.

[0026]

When an intermediate layer composed mainly of indium oxide is provided on the interface with the photovoltaic element, on the other hand, shunt
5 resistance tends to decrease to deteriorate the Voc and FF values depending on conditions under which zinc oxide is produced, content of a dopant, e.g., tin, its resistivity and thickness, among others. The decreased shunt resistance conceivably results from generation of
10 leakage current flowing in the intermediate layer in the lateral direction, because indium oxide generally has a lower resistivity than that of zinc oxide. Moreover, indium oxide is more sensitive to a reducing atmosphere than zinc oxide, and indium separates out
15 when a photovoltaic element is formed on indium oxide, thereby deteriorating the characteristics, including long-term reliability.

[0027]

No deterioration of the characteristics, in
20 particular Voc and FF, is observed, when a thin, first layer mainly composed of indium oxide and then second layer mainly composed of zinc oxide are stacked on the interface with the photovoltaic element to form the intermediate layer. This conceivably results from the
25 improved interface between the first layer and photovoltaic element, although not fully substantiated. It is expected that flowing of leakage current in the

lateral direction can be made difficult when the first layer has an adequate resistivity and thickness, and photocurrent can be increased when the second layer is adequately thick.

5 [0028]

The first layer preferably has a sufficient resistivity so as to make difficult the flowing of leakage current in the lateral direction and is adequately thin. The photovoltaic element is attached
10 frequently at high temperature, and indium can diffuse when exposed to high temperature continuously for extended periods to deteriorate the characteristics including long-term reliability. It is preferable, also viewed from the above, the first layer is
15 adequately thin. Therefore, the first layer mainly composed of indium oxide preferably has a thickness of 1 nm or more and 50 nm or less, more preferably 3 nm or more and 40 nm or less, still more preferably 5 nm or more and 30 nm or less.

20 [0029]

The intermediate layer, on the other hand, reflects more light to the photovoltaic element provided thereon as its thickness increases. Therefore, the second layer is preferably thicker than
25 the first layer.

[0030]

The first layer preferably has a lower resistivity

than the second layer. Each layer preferably has an average transmittance of 80% or more for the visible light, in particular the transmittance of 80% or more at a wavelength of 800 nm (light of long wavelength
5 side). Moreover, the second layer preferably has a higher transmittance at a wavelength of 800 nm than the first layer.

[0031]

As discussed above, the present invention is
10 characterized by the optimum design in which at least two oxide films of different characteristics are functionally separated from each other in accordance with the characteristics of each film.

[0032]

15 The intermediate layer has a certain thickness. The increase of a deposition rate is economically advantageous because of decreased tact time, but is liable to deteriorate the characteristics. Formation of the first layer at a lower rate can secure the good
20 interfacial characteristics while minimizing the damages. No deterioration of the characteristics is observed, when the first layer is formed at a lower rate and then the second layer at a higher rate. Therefore, the second layer is preferably formed at a
25 higher rate than the first layer.

[0033]

Moreover, indium tends to diffuse, and hence the

intermediate layer is preferably formed at as low temperature as possible after the first layer is formed. It should be noted, however, that decreasing deposition temperature tends to deteriorate the transmittance of indium oxide. Therefore, a certain temperature level is essential for forming the indium oxide layer. The zinc oxide layer, on the other hand, tends to have a higher transmittance to have the enhanced Jsc value, when formed at lower temperature. Increasing deposition temperature, however, generates more stress in the zinc oxide layer, tending to cause separation of the stacked structure at the intermediate layer. Therefore, the second layer is preferably formed at a lower temperature than the first layer. The first layer is preferably formed at 150°C or higher but 300°C or lower, and the second layer at 50°C or higher but 250°C or lower. Moreover, the second layer is more preferably formed at a temperature lower by at least 40°C.

[0034]

Next, the construction of the stacked photovoltaic element of the present invention will be described.

[0035]

Fig. 2 schematically outlines a cross-sectional structure of one embodiment of the stacked photovoltaic element of the present invention. The stacked photovoltaic element has on the electroconductive

substrate 201 of a metal or the like, the light reflection layer 202, second photovoltaic element 203, the intermediate layer 206 (consisting of the first layer 204 mainly composed of indium oxide and the
5 second layer 205 mainly composed of zinc oxide), first photovoltaic element 207 and transparent electrode 208 stacked in this order as shown in Fig. 2. It is designed in such a way that a semiconductor which constitutes the photoactive section for the first
10 photovoltaic element 207 has a larger band gap than a semiconductor which constitutes the photoactive section for the second photovoltaic element 203, or the photoactive section of the former is made thinner than the latter, thereby allowing the first photovoltaic
15 element 207 to absorb light in a short wavelength range while allowing the second photovoltaic element 203 to absorb light in a long wavelength range. The intermediate layer 206 functions to reflect a part of light and thereby to increase quantity of light
20 absorbed by the first photovoltaic element 207. The intermediate layer 206 may be provided with irregularities on the surface.

[0036]

Fig. 1 schematically outlines the method of the
25 present invention for producing the stacked photovoltaic element of the present invention as shown in Fig. 2.

[0037]

On the substrate 100 having a reflection layer 101 and second photovoltaic element 102 formed thereon as shown in (a) of Fig. 1, a layer 103 mainly composed of indium oxide is deposited as shown in (b) of Fig. 1. The layer 104 mainly composed of zinc oxide is deposited as shown in (c) of Fig. 1. The first photovoltaic element 106 is further deposited thereon as shown in (d) of Fig. 1. Then, the transparent electrode is deposited thereon. The deposition of each layer in this order complete the stacked photovoltaic element with the intermediate layer 105 (consisting of the layer 103 mainly composed of indium oxide and layer 104 mainly composed of zinc oxide) between the photovoltaic elements.

[0038]

Fig. 3 schematically outlines a cross-sectional structure of another embodiment of the stacked photovoltaic element of the present invention. The stacked photovoltaic element has on the transparent, insulating substrate 301 of glass or the like, transparent electrode 308, first photovoltaic element 307, intermediate layer 306 (consisting of the first layer 304 mainly composed of indium oxide and second layer 305 mainly composed of zinc oxide), second photovoltaic element 303 and electroconductive, light reflection layer 302 stacked in this order. In this

case, incident light enters the stacked photovoltaic element from the transparent, insulating substrate 301 side. The intermediate layer 306 may be provided with irregularities on the surface.

5 [0039]

Next, each component for the stacked photovoltaic element of the present invention is described.

[0040]

(Substrate)

10 The material for the substrate which constitutes the stacked photovoltaic element of the present invention is not limited. It may be an electroconductive or insulating material of any type. The electroconductive materials include metals, e.g.,
15 plated steel, NiCr, stainless steel, Al, Cr, Mo, Au, Nb, Ta, V, Ti, Pt, Pb, Sn and an alloy thereof. The insulating materials include synthetic resins, e.g., polyester, polyethylene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride,
20 polyvinylidene chloride, polystyrene and polyamide; and glass, ceramics and paper. The particularly preferable materials are stainless steel as the metal substrate, and glass, ceramics and polyimide as the insulating substrate. A transparent, insulating substrate is used
25 for the stacked photovoltaic element with incident light entering from the substrate side, and glass is suitable for the substrate.

[0041]

The substrate surface may be smooth or of irregular texture with irregularities having the maximum height of 0.1 to 1.0 μm . A stainless steel
5 substrate may have a surface of irregular texture by etching with an acidic solution.

[0042]

Thickness of the substrate may be adequately set to give a desired stacked photovoltaic element by
10 stacking the layers one on another as intended. When the stacked photovoltaic element is required to be flexible, it may be as thin as possible so long as it can sufficiently work as a support. However, it normally has a thickness of 10 μm or more in
15 consideration of production, handling and mechanical strength.

[0043]

(Reflection Layer)

The reflection layer for the stacked photovoltaic
20 element of the present invention is made of a deposited film of a metal which has a high reflectivity of light from the visible to near-infrared ray, e.g., Ag, Al, Cu and an alloy thereof. It is suitably formed by, e.g., vacuum evaporation, sputtering or electrolytic
25 deposition from an aqueous solution. It is preferably 10 to 5000 nm thick. It is preferably provided with irregularities on the surface for irregular reflection.

It is also preferably provided with an increased reflectance layer to increase quantity of reflected light.

[0044]

5 The materials for the increased reflectance layer include ZnO, SnO₂, In₂O₃, ITO, TiO₂, CdO, Cd₂SnO₄, Bi₂O₃, MoO₃ and Na_xWO₃. The increased reflectance layer is suitably formed by vacuum evaporation, sputtering, electrolytic deposition, CVD, spraying, spin-on, 10 dipping or the like of the above material. Its thickness is preferably 50 nm to 10 μm, although the optimum thickness varies depending on inherent reflectivity of the material used. The increased reflectance layer is preferably provided with 15 irregularities on the surface for increasing light scattering. For example, in the sputtering method sputtering conditions may be selected to provide irregularities based on the grain boundaries.

[0045]

20 (Photovoltaic Element)

 The semiconductors useful for the stacked photovoltaic element of the present invention include single-crystalline, poly-crystalline, microcrystalline and amorphous materials of IV, III-V, II-VI, I-III-VI₂ 25 groups. The IV group materials include C, Si and Ge and an alloy thereof, III-V group materials AlAs, AlSb, GaN, GaP, GaAs, GaSb, InP and InAs, II-VI group

materials ZnSe, ZnS, ZnTe, CdS, CdSe, CdTe and Cu₂S,
and I-III-VI₂ group materials CuInSe₂. Of these,
silicon-based semiconductors are more preferable. The
single-crystalline, poly-crystalline, microcrystalline
5 and amorphous semiconductors are suitably used.

[0046]

The photovoltaic element containing a PN- or PIN-
junction for the stacked photovoltaic element of the
present invention contains a PN- or PIN-junction and
10 comprises at least two photovoltaic layers. The
semiconductors for these photovoltaic elements may be
the same or different material. However, in the
preferable structure, a photovoltaic element using a
semiconductor which can more efficiently absorb light
15 of shorter wavelengths and another photovoltaic element
using a semiconductor which can more efficiently absorb
light of longer wavelengths are stacked in this order
from the incident light side, because light of shorter
wavelength is more easily absorbed.

20 [0047]

(Intermediate Layer)

The intermediate layer for the stacked
photovoltaic element of the present invention comprises
two layers, one being mainly composed of indium oxide
25 and the other mainly composed of zinc oxide. The layer
mainly composed of indium oxide may contain a trace
quantity of another component, e.g., Mg, Zn, Sn or Sb.

[0048]

The layer mainly composed of zinc oxide may contain a trace quantity of another component, e.g., Al, Sn, In, Fe, Ga, Co, Si, Ti, Ge or Sb.

5 [0049]

The intermediate layer may contain a still another component, e.g., SnO_2 , TiO_2 , CdO , Cd_2SnO_4 , Bi_2O_3 , MoO_3 or Na_xWO_3 .

[0050]

10 The intermediate layer may be suitably formed by vacuum evaporation, sputtering, electrolytic deposition, CVD, spraying, spin-on, dipping or the like.

[0051]

15 The intermediate layer formed may be further treated by wet etching, dry etching or the like to have irregularities on the surface. It is formed by stacking the layer mainly composed of indium oxide on the interface with the semiconductor and then the layer
20 mainly composed of zinc oxide.

[0052]

(Transparent Electrode)

The materials for the transparent electrode for the stacked photovoltaic element of the present
25 invention include indium oxide, tin oxide, indium-tin oxide or zinc oxide. The transparent electrode is formed by sputtering, vacuum evaporation, chemical

vapor deposition, ion plating, ion beam or ion beam sputtering. It may be also formed by electrolytic deposition or immersion in an aqueous solution of a metallic ion, e.g., that containing nitric, acetic or ammonia group. It preferably has a sufficient thickness to satisfy the requirements as an antireflection film.

[0053]

[Examples]

10 The examples as the preferred embodiments of the present invention are described in detail by referring to the attached drawings. It should be understood that the present invention is not limited to these examples.

[0054]

15 [Example 1]

 In Example 1, the stacked photovoltaic element of the third aspect of the present invention comprising a PIN-type photovoltaic element with the i-type layer of intrinsic amorphous Si:H as the first photovoltaic element, a PIN-type photovoltaic element with the i-type layer of intrinsic microcrystalline Si as the second photovoltaic element, and an intermediate layer of indium/tin oxide and zinc oxide was produced as shown in Fig. 2.

25 [0055]

 Referring to Fig. 2, the substrate 201, 45 mm square and 0.15 mm thick, was of flat stainless steel

(SUS 430), commonly referred to as BA-finished one. It was put in a commercial DC magnetron sputtering unit (not shown), which was evacuated to a pressure of 10^{-3} Pa or less.

5 [0056]

Argon was supplied into the unit at $30 \text{ cm}^3/\text{min}$ (normal conditions) to keep pressure inside at 2×10^{-1} Pa. A DC power of 120 W was applied to an aluminum target (diameter: 6 inches) for 90 seconds to form a
10 thin film of aluminum with a thickness of 70 nm on the substrate, while the substrate was kept unheated. Then, a DC power of 500 W was applied to a zinc oxide target (diameter: 6 inches), after the electrical connection was changed, for 30 minutes to form the
15 increased reflectance layer of zinc oxide with a thickness of about 3000 nm on the substrate 201, while the substrate was kept at 200°C .

[0057]

Fig. 4 schematically illustrates one embodiment of
20 suitable apparatus for producing a semiconductor layer for the stacked photovoltaic element of the present invention, where the deposited film forming apparatus 500 comprises the following major components; 501: load chamber, 502: RF chamber for the n-type layer, 503:
25 chamber for the i-type layer of microcrystalline silicon, 504: RF chamber for the i-type layer of amorphous silicon, 505: RF chamber for the p-type layer

and 506: unload chamber. These chambers are isolated from each other by a gate valve 507, 508, 509, 510 or 511 so that feed gases of the respective chambers are not mixed with each other.

5 [0058]

The chamber 503 for the i-type layer of microcrystalline silicon is composed of the heater 512 for heating the substrate and plasma CVD chamber 513. The RF chamber 502 is composed of the heater 514 for
10 depositing the n-type layer and deposition chamber 515 for depositing the n-type layer, the RF chamber 504 the heater 516 for depositing the i-type layer and deposition chamber 517 for depositing the i-type layer, and the RF chamber 505 the heater 518 for depositing
15 the p-type layer and deposition chamber 519 for depositing the p-type layer. The substrate is supported by the substrate holder 521 to run on the rail 520 by a roller driven from an outside power source. In the plasma CVD chamber 513, a microcrystal
20 is deposited by microwave plasma CVD or VHF plasma CVD.
[0059]

The deposited film forming apparatus of the above structure was used to form the photovoltaic elements under the given deposition conditions given in Table 1.

25 [0060]

[Table 1]

		Gas for layer formation (cm ³ /minute under normal conditions)				Power density (W/cm ²)		Pressure (Pa)	Substrate temperature (°C)	Thickness of layer (nm)
		SiH ₄	H ₂	PH ₃ (diluted to 2% with H ₂)	BF ₃ (diluted to 2% with H ₂)	RF	VHF			
First photovoltaic element	N1	2	48	0.5		0.04		180	225	10
	i1	2	48			0.04		150	210	500
	P1	0.025	35		1	1.2		270	165	5
Second photovoltaic element	N2	2	48	0.5		0.04		180	225	20
	i2	25	750				0.2	40	250	2000
	P2	0.025	35		1	1.2		270	165	5

[0061]

First, the second photovoltaic element was formed on the substrate 201 under the conditions given in Table 1 by the following procedure. The substrate 201
5 was set on the substrate holder 521 and then on the rail 520 in the load chamber 501. The load chamber 501 was then evacuated to a vacuum of several hundreds mPa or less.

[0062]

10 Next, the gate valve 507 was opened, and the substrate holder 521 was moved into the deposition chamber 515 for depositing the n-type layer in the chamber 502, where the n-type layer was deposited to a given thickness using a given feed gas, while the gate
15 valves 507, 508, 509, 510 and 511 were kept closed. The chamber 502 was sufficiently evacuated, and the gate valve 508 was opened to move the substrate holder 521 into the deposition chamber 503. Then the gate valve 508 was closed.

20 [0063]

The substrate was heated to a given temperature by the heater 512, and a necessary quantity of the feed gas was charged in the chamber. Given microwave or VHF energy was introduced into the deposition chamber 513,
25 which was evacuated to a given vacuum level, to generate a plasma therein to deposit the i-type layer of microcrystalline silicon to a given thickness on the

substrate. The chamber 503 was sufficiently evacuated, and the gate valves 509 and 510 were opened to move the substrate holder 521 from the chamber 503 to the chamber 505.

5 [0064]

After the substrate holder 521 was moved into the deposition chamber 519 for depositing the p-type layer in the chamber 505, the substrate was heated to a given temperature by the heater 518. A necessary quantity of
10 the feed gas to deposit the p-type layer was charged in the deposition chamber 519, in which RF energy was supplied to deposit the p-type layer to a given thickness, while the chamber was kept at a given vacuum level.

15 [0065]

Similarly, the chamber 519 was sufficiently evacuated, and the gate valve 511 was opened to move the substrate holder 521 having the substrate 201 with a stacked photovoltaic element into the unload chamber
20 506.

[0066]

Then, the substrate was cooled with nitrogen gas charged in the unload chamber 506, while all of the gate valves were closed. Then, the substrate holder
25 521 was taken out of the unload chamber 506, after the discharge valve was opened.

[0067]

Next, the substrate 201, on which the layers up to the second photovoltaic element were formed, was removed from the substrate holder 521 and set in a commercial DC magnetron sputtering apparatus (not shown) in order to form the immediate layer. Then, the apparatus was evacuated to a pressure of 10^{-3} Pa or less.

[0068]

Indium/tin oxide was sputtered onto the substrate with a mixed of tin oxide (3% by weight) and indium oxide (97% by weight) as the target.

[0069]

It was deposited under the conditions of substrate temperature: 170°C , argon gas (as an inert gas) flow rate: $50\text{ cm}^3/\text{minute}$ (normal conditions), oxygen gas flow rate: $0.2\text{ cm}^3/\text{minute}$ (normal conditions) and pressure in the deposition chamber: 200 mPa, where a DC power of 10 W was applied for about 100 seconds to deposit the layer to a thickness of about 10 nm after the electrical connection was changed to the indium/tin oxide target (diameter: 6 inches). Thickness of the layer was estimated by the predetermined relationship between thickness and deposition time.

[0070]

Then, the zinc oxide layer was deposited by sputtering in the same apparatus, after the target was changed to that of zinc oxide.

[0071]

It was deposited under the conditions of argon gas flow rate: 30 cm³/minute (normal conditions), oxygen gas flow rate: 2 cm³/minute (normal conditions) and
5 pressure in the deposition chamber: 2×10^{-1} Pa, where a DC power of 100 W was applied for about 5 minutes to deposit the zinc oxide layer to a thickness of about 100 nm, after the electrical connection was changed to the zinc oxide target (diameter: 6 inches) and the
10 substrate was heated to 120°C.

[0072]

The deposited film forming apparatus 500, schematically illustrated in Fig. 4, was again used to form the PIN-type photovoltaic element of amorphous
15 Si:H as the first photovoltaic element on the substrate 201 provided with the intermediate layer by the following procedure.

[0073]

The n-type layer was deposited to a given
20 thickness under given conditions in the chamber 502 in a manner similar to that described above. The gate valves 508 and 509 were opened, after the chamber 502 was sufficiently evacuated, and the substrate holder 521 was moved into the chamber 504. Then, these valves
25 were closed.

[0074]

The substrate was heated to a given temperature by

the heater 516, and a necessary quantity of the feed gas was charged in the chamber. Given RF energy was introduced into the deposition chamber 517, which was evacuated to a given vacuum level, to generate a plasma
5 therein to deposit the i-type layer of amorphous Si:H to a given thickness. The chamber 504 was sufficiently evacuated, and the gate valve 510 was opened to move the substrate holder 521 from the chamber 504 to the chamber 505.

10 [0075]

The p-type layer was deposited to a given thickness in the chamber 505 in a manner similar to that described above.

[0076]

15 Similarly, the deposition chamber 519 was sufficiently evacuated, and the gate valve 511 was opened to move the substrate holder 521, which supported the substrate 201 provided with the photovoltaic element, into the unload chamber 506.

20 [0077]

Then, the substrate holder 521 was taken out of the unload chamber 506 in a manner similar to that described above.

[0078]

25 Next, the substrate was set on the anode surface of a DC magnetron sputtering apparatus, and masked with stainless steel. Indium/tin oxide was sputtered onto

the substrate in a center area of a 40 by 40 mm from a target composed of tin oxide (10% by weight) and indium oxide (90% by weight) as the transparent electrode.

[0079]

5 The oxide film was deposited to 70 nm under the conditions of substrate temperature: 170°C, argon (as an inert gas) flow rate: 50 cm³/minute (normal conditions), oxygen gas flow rate: 0.5 cm³/minute (normal conditions), pressure in the deposition
10 chamber: 300 mPa, power density on the unit target area: 0.2W/cm² and deposition time: about 100 seconds. Thickness of the film was estimated by the predetermined relationship between thickness and deposition time. The stacked photovoltaic element
15 sample thus prepared was named "Ex. 1".

[0080]

[Comparative Example 1]

 The stacked photovoltaic element 400 was prepared to have the same structure as that of the stacked
20 photovoltaic element 200 of the present invention, except that the intermediate layer 406 was composed of only one layer as shown in Fig. 7. Referring to Fig. 7, on the electroconductive substrate 401 of a metal or the like, the light reflection layer 402, second
25 photovoltaic element 403, intermediate layer 406, first photovoltaic element 407 and transparent electrode 408 were stacked in this order.

[0081]

The zinc oxide layer as the intermediate layer 406 was deposited by sputtering with a target of zinc oxide.

5 [0082]

It was deposited under the conditions of argon gas flow rate: 30 cm³/minute (normal conditions), oxygen gas flow rate: 2 cm³/minute (normal conditions) and pressure in the deposition chamber: 2×10^{-1} Pa, where a DC power of 100 W was applied for about 5 minutes and 30 seconds to deposit the zinc oxide layer to a thickness of about 110 nm, after the electrical connection was changed to the zinc oxide target (diameter: 6 inches) and the substrate was heated to 100°C. The stacked photovoltaic element was prepared in the same manner as in Example 1, except that the intermediate layer 406 composed of only one layer was used. This sample was named "Compar. 1-1".

[0083]

20 In deposition of the intermediate layer 406, indium/tin oxide was sputtered onto the substrate using a target composed of tin oxide (3% by weight) and indium oxide (97% by weight).

[0084]

25 The intermediate layer was deposited to about 110 nm under the conditions of substrate temperature: 170°C, argon (as an inert gas) flow rate: 50 cm³/minute

(normal conditions), oxygen gas flow rate: 0.2
cm³/minute (normal conditions), pressure in the
deposition chamber: 200 mPa, where a DC power of 10 W
was applied for about 18 minutes and 20 seconds, after
5 the electrical connection was changed to the target of
indium/tin oxide (diameter: 6 inches). The stacked
photovoltaic element was prepared in the same manner as
in Example 1, except that the intermediate layer 406
prepared above was used. This sample was named
10 "Compar. 1-2".

[0085]

Moreover, in preparation of the intermediate layer
206 for the stacked photovoltaic element 200
illustrated in Fig. 2, zinc oxide was sputtered first
15 with a target of zinc oxide.

[0086]

It was deposited under the conditions of argon gas
flow rate: 30 cm³/minute (normal conditions), oxygen
gas flow rate: 2 cm³/minute (normal conditions) and
20 pressure in the deposition chamber: 2×10^{-1} Pa, where a
DC power of 100 W was applied for about 30 minutes to
deposit the zinc oxide layer to a thickness of about 10
nm, after the electrical connection was changed to the
zinc oxide target (diameter: 6 inches) and the
25 substrate was heated to 120°C.

[0087]

Then, indium/tin oxide was sputtered in the same

apparatus, after the target was changed to a target composed of tin oxide (3% by weight) and indium oxide (97% by weight).

[0088]

5 The intermediate layer was deposited to about 100 nm under the conditions of substrate temperature: 170°C, argon (as an inert gas) flow rate: 50 cm³/minute (normal conditions), oxygen gas flow rate: 0.2 cm³/minute (normal conditions), pressure in the
10 deposition chamber: 200 mPa, where a DC power of 10 W was applied for about 16 minutes and 40 seconds, after the electrical connection was changed to the target of indium/tin oxide (diameter: 6 inches). The stacked photovoltaic element was prepared in the same manner as
15 in Example 1, except that the intermediate layer prepared above was used. This sample was named "Compar. 1-3".

[0089]

 These samples prepared in Example 1 and
20 Comparative Example 1 were measured for the current-voltage characteristics while they were irradiated with light under the conditions of AM1.5 spectral pattern and intensity of 100 mW/cm² using an analyzer (YSS-150 manufactured by Yamashita Denso company), and their
25 short-circuit current density J_{sc} (mA/cm²), open voltage V_{oc} (V) and fill factor FF were estimated based on these characteristics to determine conversion

efficiency $\eta(\%)$.

[0090]

Shunt resistance R_{sh} ($k\Omega cm^2$) was also estimated based on the current-voltage characteristics under a dark condition from the slope at near the origin.

[0091]

These results are given in Table 2 by the ratio of characteristic values of Example to those of Comparative Example (Ex. 1/Compar. 1-1, Ex. 1/Compar. 1-2 and Ex. 1/Compar. 1-3).

[0092]

[Table 12]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 1/ Compar. 1-1	1.001	1.017	1.044	1.064	8.20×10^{-1}
Ex. 1/ Compar. 1-2	1.014	1.152	1.006	1.174	1.54×10^2
Ex. 1/ Compar. 1-3	1.013	1.156	1.051	1.231	9.23×10^1

[0093]

Ex. 1 exhibited a higher conversion efficiency than Compar. 1-1 resulting from improvements both in the FF and Voc values. Fig. 5 shows JV curves of these samples. Superiority of Ex. 1 mainly resulted from the improved Voc value, conceivably indicating that Compar. 1-1 had a defective junction between the interface with the semiconductor and that with the intermediate layer.

[0094]

Ex. 1 exhibited a higher conversion efficiency than Compar. 1-2 resulting from improvements in all of the FF, Voc and Rsh values. Fig. 6 shows JV curves of these samples. Superiority of Ex. 1 mainly resulted from decreased shunt resistance of Compar. 1-2, which mainly decreased the FF value.

[0095]

Ex. 1 exhibited a higher conversion efficiency than Compar. 1-3 resulting from improvements in all of the FF, Voc and Rsh values. Compar. 1-3 was formed by depositing zinc oxide and then indium/tin oxide in this order which was reversed in Ex. 1. This order conceivably deteriorated the interfacial junction conditions and shunt resistance, which in turn caused the decreased Voc and FF values.

[0096]

The reliability test was conducted by the following procedure. A reverse bias of -0.85 V was applied continuously for 20 hours to the sample kept at 85°C and 85% RH in a high-temperature, high-humidity chamber. It was then taken out of the chamber, and naturally dried and cooled sufficiently to be analyzed for the voltage-current characteristics. The results are given in Table 3, where each of the characteristics reported is relative to the initial level.

[0097]

[Table 3]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 1	1.001	0.991	0.997	0.989	0.785
Compar. 1-1	1.000	0.989	0.998	0.987	0.779
Compar. 1-2	0.959	0.906	0.992	0.862	0.387
Compar. 1-3	0.980	0.947	0.995	0.924	0.449

[0098]

The reliability test caused essentially no decrease in shunt resistance with respect to both Ex. 1 and Compar. 1-1, whereas it decreased the value from the initial level with respect to Compar. 1-2 and 1-3, mainly resulting in the decreased Voc and FF values to cause deteriorated photoelectric conversion efficiency.

[0099]

It is therefore concluded, based on the above results, that the present invention has good initial photoelectric conversion efficiency and are highly durable.

[0100]

[Example 2]

In Example 2, the stacked photovoltaic element of the present invention comprising the PIN-type photovoltaic element with the i-type layer of intrinsic amorphous Si:H as the first photovoltaic element, PIN-type photovoltaic element with the i-type layer of intrinsic microcrystalline Si as the second photovoltaic element, and the intermediate layer of

indium/tin oxide and zinc oxide was produced, where three samples of varying the thickness ratio of the indium/tin oxide layer to zinc oxide layer were prepared.

5 [0101]

For preparation of the intermediate layer, indium/tin oxide was sputtered onto the substrate using a target composed of tin oxide (3% by weight) and indium oxide (97% by weight).

10 [0102]

Indium/tin oxide was deposited under the conditions of substrate temperature: 170°C, argon gas (as an inert gas) flow rate: 50 cm³/minute (normal conditions), oxygen gas flow rate: 0.2 cm³/minute (normal conditions) and pressure in the deposition chamber: 200 mPa, where a DC power of 10 W was put for a given time to deposit the layer to a given thickness after the electrical connection was changed to the indium/tin oxide target (diameter: 6 inches).

20 [0103]

Then, the zinc oxide layer was deposited by sputtering in the same apparatus, after the target was changed to that of zinc oxide.

[0104]

25 Zinc oxide was deposited under the conditions of argon gas flow rate: 30 cm³/minute (normal conditions), oxygen gas flow rate: 2 cm³/minute (normal conditions)

and pressure in the deposition chamber: 2×10^{-1} Pa,
where a DC power of 100 W was applied for a given time
to deposit the layer to a given thickness, after the
electrical connection was changed to the zinc oxide
5 target (diameter: 6 inches) and the substrate was
heated to 120°C. All of these intermediate layers have
the same total thickness set at about 110 nm.

[0105]

These stacked photovoltaic element samples were
10 prepared in the same manner as in Example 1, except
that thickness ratio of the indium/tin oxide layer to
zinc oxide layer was varied. These samples were named
"Ex. 2A", "Ex. 2B", "Ex. 2C" and "Ex. 2D". Table 4
summarizes the conditions under which each sample was
15 prepared.

[0106]

[Table 4]

	Indium tin oxide		Zinc oxide	
	Deposition time	Thickness of layer (nm)	Deposition time	Thickness of layer (nm)
Ex. 2A	1 min. 40 sec.	10	5 min.	100
Ex. 2B	7 min. 30 sec.	45	3 min. 15 sec.	65
Ex. 2C	10 min. 50 sec.	65	2 min. 15 sec.	45
Ex. 2D	16 min. 40 sec.	100	30 sec.	10

[0107]

Next, each photovoltaic element was analyzed for its current-voltage characteristics in the same manner as in Example 1. The results are given in Table 5, where each of the characteristics is relative to that of Compar. 1-2.

[0108]

[Table 5]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 2A/ Compar. 1-2	1.014	1.152	1.006	1.174	1.54×10^2
Ex. 2B/ Compar. 1-2	1.013	1.147	1.006	1.169	3.11×10^1
Ex. 2C/ Compar. 1-2	1.010	1.078	1.001	1.090	1.57×10^1
Ex. 2D/ Compar. 1-2	1.009	1.023	0.999	1.031	2.18×10^0

[0109]

Each of Ex. 2A, Ex. 2B, Ex. 2C and Ex. 2D had better characteristics than Compar. 1-2. It was also
5 observed that conversion efficiency increased as the thickness of the indium/tin oxide layer became smaller than that of the zinc oxide layer. The reliability test was also conducted in the same manner as in Example 1. The results are given in Table 6, where
10 each of the characteristics reported is relative to the initial level.

[0110]

[Table 6]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 2A	1.001	0.991	0.997	0.989	0.785
Ex. 2B	0.999	0.997	1.000	0.996	0.899
Ex. 2C	0.982	0.910	1.000	0.894	0.240
Ex. 2D	0.963	0.903	0.999	0.870	0.298
Compar. 2-2	0.959	0.906	0.992	0.862	0.387

[0111]

The reliability test results indicated that each of Ex. 2A, Ex. 2B, Ex. 2C and Ex. 2D had higher
5 reliability than Compar. 1-2. It was also observed that reliability increased as the thickness of the indium/tin oxide layer became smaller than that of the zinc oxide layer.

[0112]

10 To summarize these results: Ex. 2A and Ex. 2B have a higher conversion efficiency and higher reliability than Ex. 2C and Ex. 2D, and the indium/tin oxide layer is preferably thinner than the zinc oxide layer.

[0113]

15 [Example 3]

In Example 3, the stacked photovoltaic element of the present invention comprising the PIN-type photovoltaic element with the i-type layer of intrinsic amorphous Si:H as the first photovoltaic element, the
20 PIN-type photovoltaic element with the i-type layer of intrinsic microcrystalline Si as the second

photovoltaic element, and the intermediate layer of indium/tin oxide and zinc oxide was produced, where four samples of varying the thickness ratio of the indium/tin oxide layer to zinc oxide layer were
5 prepared.

[0114]

For preparation of the intermediate layer, indium/tin oxide was sputtered onto the substrate using a target composed of tin oxide (3% by weight) and
10 indium oxide (97% by weight).

[0115]

Indium/tin oxide was deposited under the conditions of substrate temperature: 170°C, argon gas (as an inert gas) flow rate: 50 cm³/minute (normal
15 conditions), oxygen gas flow rate: 0.2 cm³/minute (normal conditions) and pressure in the deposition chamber: 200 mPa, where a DC power of 10 W was put for a given time to deposit the layer to a given thickness after the electrical connection was changed to the
20 indium/tin oxide target (diameter: 6 inches).

[0116]

Then, the zinc oxide layer was deposited by sputtering in the same apparatus, after the target was changed to that of zinc oxide.

25 [0117]

Zinc oxide was deposited under the conditions of argon gas flow rate: 30 cm³/minute (normal conditions),

oxygen gas flow rate: 2 cm³/minute (normal conditions)
and pressure in the deposition chamber: 2×10⁻¹ Pa,
where a DC power of 100 W was applied for 5 minutes to
deposit the layer to a thickness of 100 nm, after the
5 electrical connection was changed to the zinc oxide
target (diameter: 6 inches) and the substrate was
heated to 120°C. These stacked photovoltaic element
samples were prepared in the same manner as in Example
1, except that thickness of the indium/tin oxide layer
10 for the intermediate layer was varied. These samples
were named "Ex. 3A", "Ex. 3B", "Ex. 3C" and "Ex. 3D".
Table 7 summarizes the conditions under which each
sample was prepared.

[0118]

15 [Table 7]

	Indium tin oxide	
	Deposition time	Thickness of layer (nm)
Ex. 3A	1 min. 40 sec.	10
Ex. 3B	5	0.5
Ex. 3C	10 sec.	1
Ex. 3D	8 min. 20 sec.	50
Ex. 3E	10 min. 50 sec.	65

[0119]

Next, each photovoltaic element was analyzed for
its current-voltage characteristics in the same manner
as in Example 1. The results are given in Table 8,

where each of the characteristics is relative to that of Compar. 1-2.

[0120]

[Table 8]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 3A/ Compar. 1-2	1.001	1.017	1.044	1.064	8.20×10^{-1}
Ex. 3B/ Compar. 1-2	1.002	1.006	1.017	1.025	9.83×10^{-1}
Ex. 3C/ Compar. 1-2	1.005	1.011	1.028	1.044	8.37×10^{-1}
Ex. 3D/ Compar. 1-2	1.008	1.012	1.040	1.062	6.90×10^{-1}
Ex. 3E/ Compar. 1-2	1.008	0.997	1.040	1.045	5.82×10^{-1}

5 [0121]

Each of Ex. 2A, Ex. 2B, Ex. 2C and Ex. 2D had better characteristics than Compar. 1-1. It was also observed that the indium/tin oxide layer having a thickness in a range from 1 to 50 nm gave the stacked photovoltaic element of higher conversion efficiency. The reliability test was also conducted in the same manner as in Example 1. The results are given in Table 9, where each of the characteristics reported is relative to the initial level.

15 [0122]

[Table 9]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 3A	1.001	0.991	0.997	0.989	0.785
Ex. 3B	0.998	0.992	0.998	0.988	0.800
Ex. 3C	0.999	0.994	0.997	0.990	0.778
Ex. 3D	0.999	0.974	1.001	0.974	0.832
Ex. 3E	0.997	0.969	1.000	0.966	0.604

[0123]

The reliability test results indicated that each of Ex. 3A, Ex. 3B, Ex. 3C and Ex. 3D deteriorated in these characteristics to a limited extent. The thinner indium/tin oxide layer gave the stacked photovoltaic element of higher reliability. The indium/tin oxide layer is preferably 50 nm thick or less.

[0124]

To summarize these results: the indium/tin oxide layer having a thickness in a range from 1 to 50 nm gives the stacked photovoltaic element of higher conversion efficiency and reliability.

[0125]

[Example 4]

In Example 4, the stacked photovoltaic element of the present invention comprising the PIN-type photovoltaic element with the i-type layer of intrinsic amorphous Si:H as the first photovoltaic element, the PIN-type photovoltaic element with the i-type layer of intrinsic microcrystalline Si as the second

photovoltaic element and the intermediate layer of indium/tin oxide and zinc oxide was produced where two samples were prepared under different conditions.

[0126]

5 For preparation of the intermediate layer, indium/tin oxide was sputtered onto the substrate using a target composed of tin oxide (3% by weight) and indium oxide (97% by weight).

[0127]

10 Indium/tin oxide was deposited under the conditions of substrate temperature: 170°C, argon gas (as an inert gas) flow rate: 50 cm³/minute (normal conditions), oxygen gas flow rate: 0.2 cm³/minute (normal conditions) and pressure in the deposition
15 chamber: 200 mPa, where a DC power of 10 W was applied for 8 minutes and 20 seconds to deposit the layer to a thickness of 50 nm, after the electrical connection was changed to the indium/tin oxide target (diameter: 6 inches).

20 [0128]

 Then, the zinc oxide layer was deposited by sputtering in the same apparatus, after the target was changed to that of zinc oxide.

[0129]

25 Zinc oxide was deposited under the conditions of argon gas flow rate: 30 cm³/minute (normal conditions), oxygen gas flow rate: 2 cm³/minute (normal conditions)

and pressure in the deposition chamber: 2×10^{-1} Pa,
where a DC power of 100 W was applied for 5 minutes to
deposit the layer to a thickness of 100 nm, after the
electrical connection was changed to the zinc oxide
5 target (diameter: 6 inches) and the substrate was
heated to 120°C. These stacked photovoltaic element
samples were prepared in the same manner as in Example
1, except that thickness of the indium/tin oxide layer
for the intermediate layer was varied. This sample was
10 named "Ex. 4A".

[0130]

In a similar manner, a DC power of 35 W was
applied for 2 minutes and 30 seconds to deposit the
layer to a thickness of 50 nm, after the electrical
15 connection was changed to the indium/tin oxide target,
and then a DC power of 30 W was put for 16 minutes and
40 seconds to deposit the zinc oxide layer to a
thickness of 100 nm, after the electrical connection
was changed to the zinc oxide target. This sample was
20 named "Ex. 4B". Each sample was analyzed for its
current-voltage characteristics in the same manner as
in Example 1. The results are given in Table 10, where
each of the characteristics is relative to that of
Compar. 1-2.

25 [0131]

[Table 10]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 4A/ Compar. 1-2	1.020	1.147	1.002	1.172	1.29×10^2
Ex. 4B/ Compar. 1-2	1.020	1.133	0.996	1.151	1.57×10^2

[0132]

Ex. 4A had better characteristics than Ex.4B. The reliability test was also conducted in the same manner as in Example 1. The results are given in Table 11, where each of the characteristics reported is relative to the initial level.

[0133]

Table 11

	Jsc	FF	Voc	Eff.	Rsh
Ex. 4A	0.999	0.974	1.001	0.974	0.832
Ex. 4B	0.998	0.978	0.998	0.974	0.834
Compar. 1-2	0.959	0.906	0.992	0.862	0.387

10 [0134]

Both samples produced the good results in the reliability test.

[0135]

To summarize these results: a higher conversion efficiency and reliability can be realized, when the indium/tin oxide layer is deposited at a lower rate than the zinc oxide layer.

[0136]

[Example 5]

In Example 5, the stacked photovoltaic element of the present invention comprising the PIN-type photovoltaic element with the i-type layer of intrinsic amorphous Si:H as the first photovoltaic element, the
5 PIN-type photovoltaic element with the i-type layer of intrinsic microcrystalline Si as the second photovoltaic element, and the intermediate layer of indium/tin oxide and zinc oxide was produced where
10 three samples were prepared under different conditions.
[0137]

For preparation of the intermediate layer, indium/tin oxide was sputtered onto the substrate using a target composed of tin oxide (3% by weight) and
15 indium oxide (97% by weight).
[0138]

Indium/tin oxide was deposited under the conditions of substrate temperature: 170°C, argon gas (as an inert gas) flow rate: 50 cm³/minute (normal
20 conditions), oxygen gas flow rate: 0.2 cm³/minute (normal conditions) and pressure in the deposition chamber: 200 mPa, where a DC power of 10 W was put for 8 minutes and 100 seconds to deposit the layer to a thickness of 10 nm, after the electrical connection was
25 changed to the indium/tin oxide target (diameter: 6 inches).
[0139]

Then, the zinc oxide layer was deposited by sputtering in the same apparatus, after the target was changed to that of zinc oxide.

[0140]

5 Zinc oxide was deposited under the conditions of argon gas flow rate: 30 cm³/minute (normal conditions), oxygen gas flow rate: 2 cm³/minute (normal conditions) and pressure in the deposition chamber: 2×10⁻¹ Pa, where a DC power of 100 W was applied for 5 minutes to
10 deposit the layer to a thickness of 100 nm, after the electrical connection was changed to the zinc oxide target (diameter: 6 inches) and the substrate was heated to 120°C. These stacked photovoltaic element samples were prepared in the same manner as in Example
15 1, except that thickness of the indium/tin oxide layer for the intermediate layer was varied. This sample was named "Ex. 5A".

[0141]

 In a similar manner, a DC power of 10 W was
20 applied for 100 seconds to deposit the indium/tin oxide layer to a thickness of 10 nm while the substrate was kept at 120°C, after the electrical connection was changed to the indium/tin oxide target, and then a DC power of 100 W was put for 5 minutes to deposit the
25 zinc oxide layer to a thickness of 100 nm, after the electrical connection was changed to the zinc oxide target and the substrate was heated to 170°C. This

sample was named "Ex. 5B".

[0142]

In a similar manner, a DC power of 10 W was applied for 100 seconds to deposit the indium/tin oxide layer to a thickness of 10 nm while the substrate was kept at 170°C, after the electrical connection was changed to the indium/tin oxide target, and then a DC power of 100 W was put for 5 minutes to deposit the zinc oxide layer to a thickness of 100 nm, after the electrical connection was changed to the zinc oxide target and the substrate was heated to 250°C. This sample was named "Ex. 5C".

[0143]

Ex. 5C was visually observed to have the intermediate layer finely separated, and this was confirmed by microscopic observation.

[0144]

Each sample was analyzed for its current-voltage characteristics in the same manner as in Example 1. The results are given in Table 12, where each of the characteristics is relative to that of Compar. 1-2.

[0145]

[Table 12]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 5A/ Compar. 1-2	1.014	1.152	1.006	1.174	1.54×10^2
Ex. 5B/ Compar. 1-2	1.008	1.143	1.004	1.156	1.53×10^2
Ex. 5C/ Compar. 1-2	1.005	1.141	1.001	1.149	1.30×10^2

[0146]

Each of Ex. 5A, Ex. 5B and Ex. 5C had better characteristics than Compar. 1-2, and Ex. 5A was better than the others. The reliability test was also conducted in the same manner as in Example 1. The results are given in Table 13, where each of the characteristics reported is relative to the initial level.

10 [0147]

[Table 13]

	Jsc	FF	Voc	Eff.	Rsh
Ex. 5A	1.001	0.991	0.997	0.989	0.785
Ex. 5B	0.997	0.992	0.999	0.988	0.800
Ex. 5C	1.000	0.980	0.999	0.978	0.707
Compar. 1-2	0.959	0.906	0.992	0.862	0.387

[0148]

Each of Ex. 5A, Ex. 5B and Ex. 5C had higher reliability than Compar. 1-2.

15 [0149]

Ex. 5C had the finely separated intermediate layer, which, however, did not affect its reliability much. Ex. 5A had higher reliability than the others.

[0150]

5 To summarize these results: a higher conversion efficiency and reliability can be realized, when the zinc oxide layer was deposited at a lower temperature than the indium/tin oxide layer.

[0151]

10 [Effect of the Invention]

As explained so far, the present invention brings excellent effects, the former providing a method for producing a stacked photovoltaic element and the latter providing a stacked photovoltaic element, where the
15 stacked photovoltaic element is of high conversion efficiency, can efficiently collect energy over an entire wavelength range of incident light, and has good open-circuit voltage (Voc) and fill factor (FF).

[Brief Description of the Drawings]

20 [Fig. 1] Schematic cross-sectional views showing the method of the present invention for producing a stacked photovoltaic element.

 [Fig. 2] A schematic cross-sectional view showing the structure of one embodiment of the stacked
25 photovoltaic element of the present invention;

 [Fig. 3] A schematic cross-sectional view showing the structure of another embodiment of the stacked

photovoltaic element of the present invention;

[Fig. 4] A schematic view illustrating one
embodiment of a suitable apparatus for producing a
semiconductor layer for the stacked photovoltaic
5 element of the present invention;

[Fig. 5] An explanatory view showing J-V curves
of the stacked photovoltaic elements prepared in
Example 1 and Comparative Example 1-1.

[Fig. 6] An explanatory view showing J-V curves
10 of the stacked photovoltaic elements prepared in
Example 1 and Comparative Example 1-2.

[Fig. 7] A schematic cross-sectional view showing
the structure of the stacked photovoltaic element
having an intermediate layer composed of one layer in
15 Comparative Example.

[Description of Reference Numerals or Symbols]

100 Substrate
101 Reflection layer
102 Second photovoltaic element
20 103 Layer composed of indium oxide
104 Layer composed of zinc oxide
105 Intermediate layer
106 First photovoltaic element
200 Stacked photovoltaic element
25 201 Substrate
202 Light reflection layer
203 Second photovoltaic element

204 First layer composed of indium oxide
205 Second layer composed of zinc oxide
206 Intermediate layer
207 First photovoltaic element
5 208 Transparent electrode
300 Stacked photovoltaic element
301 Substrate
302 Light reflection layer
303 Second photovoltaic element
10 304 First layer composed of indium oxide
305 Second layer composed of zinc oxide
306 Intermediate layer
307 First photovoltaic element
308 Transparent electrode
15 400 Stacked photovoltaic element
401 Substrate
402 Light reflection layer
403 Second photovoltaic element
406 Intermediate layer
20 407 First photovoltaic element
408 Transparent electrode
500 Load chamber
502 RF chamber for n-type layer
503 Chamber for i-type layer of microcrystalline
25 silicon
504 RF chamber for i-type layer of amorphous silicon
505 RF chamber for p-type layer

506 Unload chamber
507, 508, 509, 510, 511 Gate valve
512 Heater for heating the substrate
513 Plasma CVD chamber
5 514 Heater for depositing n-type layer
515 Deposition chamber for depositing n-type layer
516 Heater for depositing i-type layer
517 Deposition chamber for depositing i-type layer
518 Heater for depositing p-type layer
10 519 Deposition chamber for depositing p-type layer
520 Rail
521 Substrate holder

[Name of the Document] Abstract

[Abstract]

[Problem(s)] It is to provide a photovoltaic element
of high conversion efficiency, capable of efficiently
5 collecting energy over an entire wavelength range of
incident light, and having good open-circuit voltage
(Voc) and fill factor (FF), among others and a method
for producing the same.

[Means for Solving the Problem(s)] It is a method for
10 producing a stacked photovoltaic element in which a
plurality of photovoltaic elements 203, 207 having a
PN- or PIN-junction are stacked and an intermediate
layer 206 is provided between the elements 203, 207 and
at least a first layer 204 mainly composed of indium
15 oxide is stacked and then a second layer 205 mainly
composed of zinc oxide is formed to form the
intermediate layer 206.

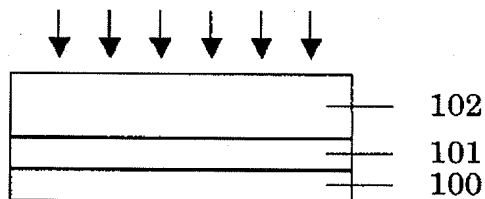
[Elected Drawing] Fig. 2

【書類名】

図面

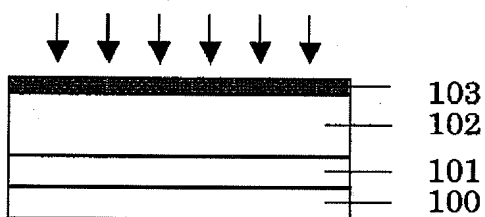
[Name of Documents] Drawings

【図1】 Fig.1



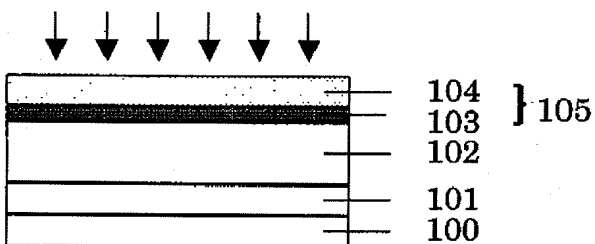
(a)酸化インジウムを含む層を堆積

A layer composed of indium oxide is deposited



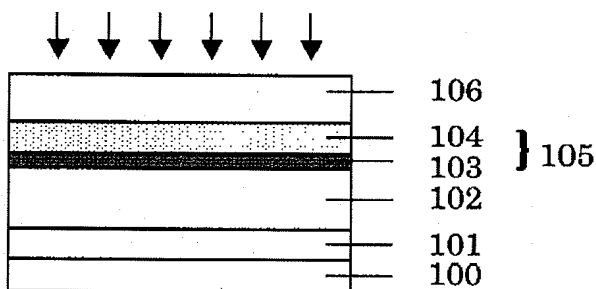
(b)酸化亜鉛を含む層を堆積

A layer composed of zinc oxide is deposited



(c)光起電力素子を堆積

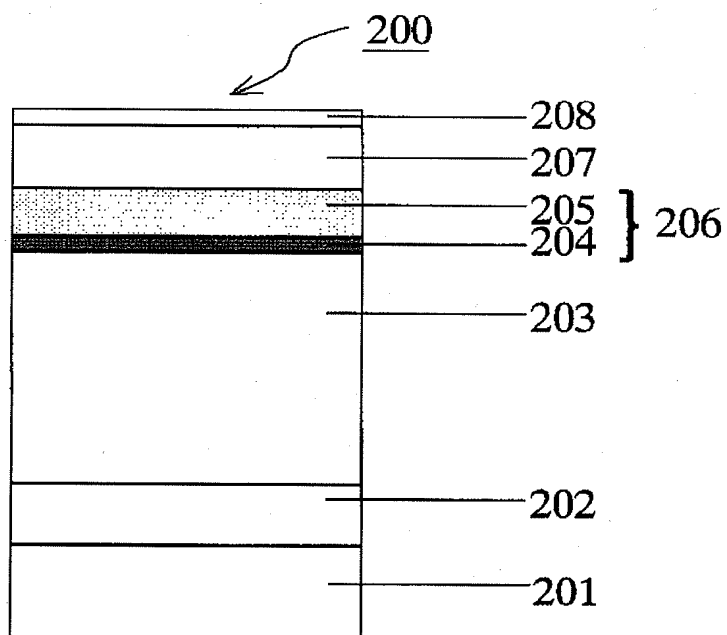
A photovoltaic element is deposited



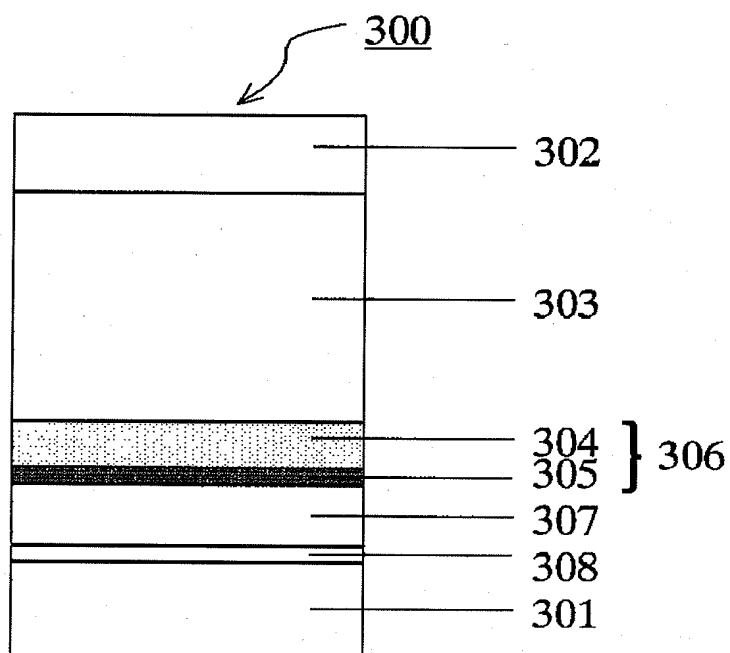
(d)透明電極を堆積

A transparent electrode is deposited

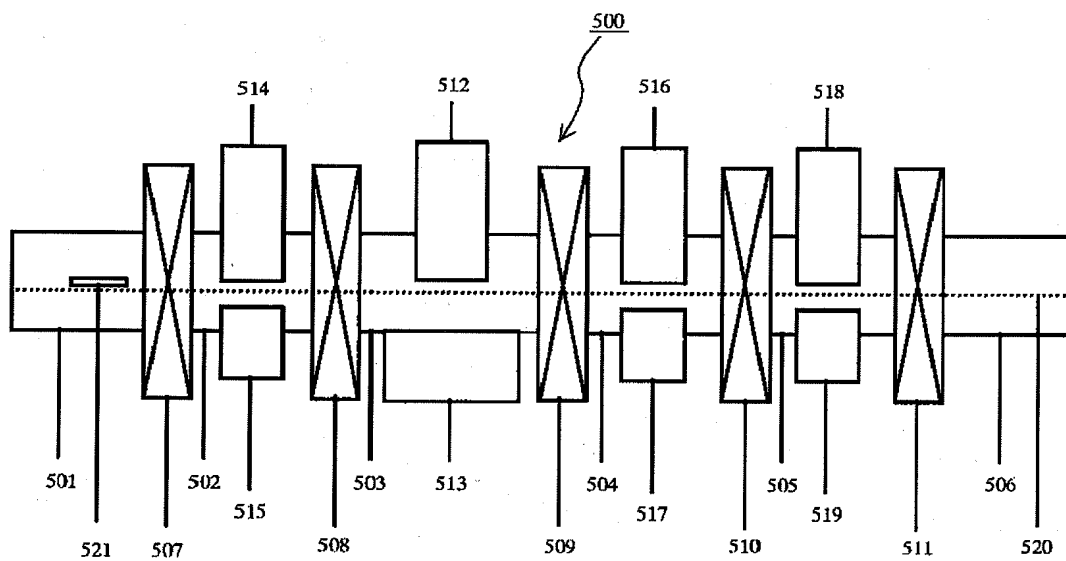
【図2】 Fig. 2



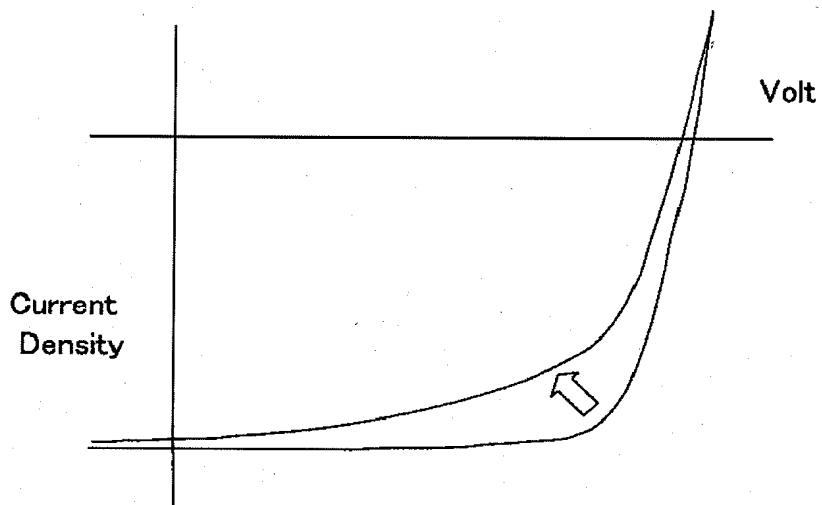
【図3】 Fig. 3



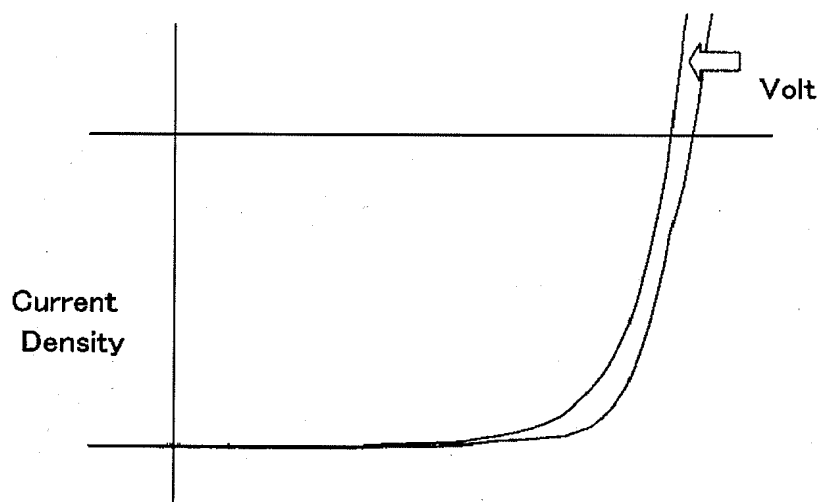
【図 4】 Fig. 4



【図 5】 Fig. 5



【図6】 Fig. 6



【図7】 Fig. 7

